FABRICATION AND CHARACTERIZATION OF CARBON NANOTUBE COMPOSITES FOR STRAIN SENSOR APPLICATIONS

G. Keulemans, F. Ceyssens, M. De Volder, J.W.Seo, R. Puers
[1]*KULeuven, dept. ESAT-MICAS, Kasteelpark Arenberg 10, 3001 Leuven, Belgium.*

Abstract **— This paper reports on the fabrication of carbon nanotube (CNT) composites based on polydimethylsiloxane (PDMS). Both composites using multiwalled carbon nanotubes (MWCNTs) as well as composites using vertically aligned carbon nanotubes (VACNTs) as conductive filler elements have been investigated. The MWCNT/PDMS composites show a quasi-linear piezoresistance response with gauge factors between 0.8 and 2.3. The VACNT/PDMS composites behave in a similar way realizing a gauge factor of 1.4. This gauge factor can be explained by only considering the geometrical change of the VACNT/PDMS composites during strain. The dense network of vertically aligned carbon nanotubes limits the contraction or tranversal strain during axial strain of the VACNT/PDMS composites. Poisson's ratio drops from 0.45 for pure PDMS to 0.2 for VACNT/PDMS composites.**
Conclusions about the suitability of these materials for use in MEMS are presented.

Keywords : **Carbon Nanotubes, CNTs, VACNTs, Strain sensors, piezoresistivity**

I - Introduction

Carbon nanotubes (CNTs) have extraordinary mechanical, electrical and thermal properties [1-3]. When used as conductive filler in polymers, CNTs not only enhance the mechanical properties but also introduce new functionality.
Indeed, conductive CNT composites are sensitive to various external stimuli, such as the chemical environment, pressure, temperature and mechanical perturbation (axial and shear stresses) [4]. The sensitivity of CNT composites enables the application of these composites as 'smart' materials in various sensors.
CNT composites have the promise to realize a higher sensitivity to strain (i.e. a higher gauge factor) in comparison to commercial strain gauges based on a meander structure of Cu − Ni or Ni − Cr [5].
This paper reports on our research aimed at the fabrication and characterization of such composites for use in sensor applications and MEMS.
The most important issues here are the efficient production of homogeneous and stable CNT composites and their piezoresistive properties.
Further important properties of CNT composites are the influence of temperature and ambient atmosphere on the conductivity, the conduction mechanism and scaling effects [6].

II - Experimental Details

A. Introduction

Polydimethylsiloxane (PDMS) is an inert silicon based polymer which has excellent hydrophobic, isolating and biocompatible properties [7]. It is also a relative low cost material.
Microfluidic MEMS applications often rely on this elastomer as a structural material. Once functionalized, its very low Young's modulus makes it interesting for use in large area flexible and stretchable devices as well. Next subsections describe the fabrication of MWCNT and VACNT composites based on PDMS.

B. MWCNT / PDMS composites.

The fabrication of MWCNT/PDMS composites relies on the common solvent evaporation method [3]. First multiwalled carbon nanotubes supplied from Nanocyl (MWCNTs grade NC7000) are mixed with the solvent tetrahydrofuran (THF) in a ratio of 300 mg MWCNTs for 20 ml THF and sonificated for 60 minutes (Branson 1510). Afterwards PDMS (Sylgard 184) from Dow Corning is added. Shear mixing (Ika Labortechnik Ultra-turrax T25) for 15 min diminishes the number of macroscopic CNT clusters still present after ultrasonification.
After shear mixing the CNT dispersion are spin coated on a Pyrex substrate to control the thickness of the composite samples. A lift-off resist (LOR30B) is needed to easily remove the MWCNT/PDMS composite after curing. Finally the free MWCNT/PDMS layers are cut in dimensions of 4 cm by 1 cm and silver epoxy contacts are applied. A plasma activation step of the surface of MWCNT/PDMS composites is necessary to guarantee a reliable electrical contact. The final MWCNT/PDMS composite samples have thicknesses between 300 and 600 µm. Figure 2 shows a photograph of a MWCNT/PDMS composite sample used during piezoresistance measurements.

Figure 1*: Photograph of MWCNT / PDMS composite test sample.*

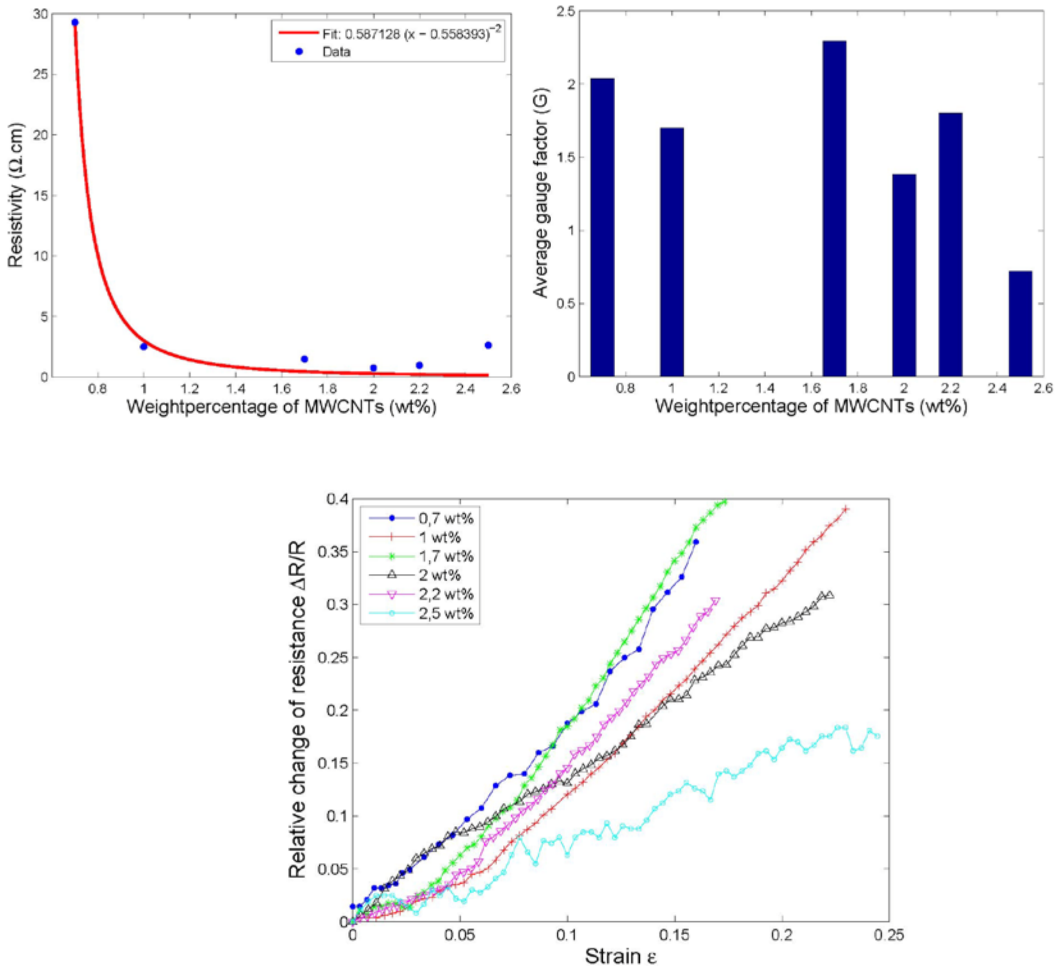

Figure 2: Measured p*iezoresistive behavior of MWCNT/PDMS composites for different weight percentages of MWCNT.*

The processing times mentioned above are derived from microscope inspection of the layers formed with the process. When no further improvement in uniformity and the presence of clusters was detected, ultrasonificiation and shear mixing times were no longer increased to limit possible breaking of the nanotubes.

C. VACNT / PDMS composites

Vertically aligned carbon nanotubes (VACNTs) have already an initial uniform distribution and alignment. VACNT composites were fabricated by drop coating the PDMS prepolymer over the VACNT forests grown by a CVD method on silicon substrates. The VACNTs have a length of 9.3 µm and a diameter of 15.6 nm. The amount of capillary induced wetting is dependent on the angle of contact between the polymer and the VACNTs, the viscosity of the polymer and the diameter and density of the VACNTs [8]. Vacuum is necessary to sufficiently wet the VACNTs and to remove remaining air bubbles in the polymer and to allow penetration of de PDMS prepolymer between the VACNTs. After curing, the VACNT/PDMS composites can be peeled off the Si substrate.

Sylgard 186 PDMS (Dow Corning) is used instead of Sylgard 184 due the better mechanical properties of former. Sylgard 184 breaks when trying to peel off the VACNT/PDMS composites for the Si substrate.

Finally silver epoxy contacts are applied after surface activation using oxygen plasma. Figure 3 shows a photograph of a VACNT/PDMS composite sample used for piezoresistance measurements.

III - Results and Discussion

A. Piezoresistivity theory

In measurements straining MWCNTs to their breaking point, no intrinsic piezoresistive behavior was found [9-10]. Therefore, the piezoresistance of MWCNTs can only be caused by charge carrier tunneling between individual CNTs [11], or by changes in the geometry of the composite layer due to the applied forces.

B. *Measurement* results

Figure 2, top left shows the measured percolation behavior of the resistance of MWCNT/PDMS composites with respect to concentration of MWCNTs (expressed as weight percentage or wt%). With our dispersion process, the percolation threshold for MWCNTs from Nanocyl MWCNTs and PDMS lies around 0.5 wt%. The relative change of the resistance of MWCNT/PDMS composites with different concentrations of MWCNTs with respect to the applied strain (ε) is shown on the bottom of in figure 2. MWCNT/PDMS composites with MWCNT concentration closer to the percolation threshold should generally have higher sensitivity for strain than MWCNT/PDMS composites with higher concentrations of MWCNTs, as explained by percolation theory.

The top right plot on figure 2 shows the average gauge factor for different concentrations of MWCNTs which lie between 0.8 and 2.3. The fact that some MWCNT/PDMS composites with a higher MWCNT concentration have a higher gauge factor than composites with a lower MWCNT concentration could be explained by an incomplete dispersion of the MWCNTs and the presence of larger clusters.

If large clusters separate due to strain, there will be a large increase in the resistance. Also the overall trend of the piezoresistive behavior is linear, in contradiction to the expected exponential dependence [4] [11]. This could also be a consequence of a nonuniform dispersion of MWCNTs.

Figure 4 shows the measured linear piezoresistive behaviour of the VACNT/PDMS composites, displaying a gauge factor of 1.4. A fit that only considers the geometrical change of the composite during strain approximates the measurement data quite well if a Poisson ratio (ν) of 0.2 is assumed. This makes sense, as the vertically aligned carbon nanotubes limit the contraction of the composite during strain, lowering the Poisson ratio with respect to standard PDMS ($\nu = 0.45$). The linear dependence can be explained the fact that the carbon nanotubes are not vertically aligned to the substrate but bent due to the high length and form contacts with multiple surrounding carbon nanotubes. Due to the high density of the carbon nanotubes only a few contacts get broken during strain.

C. *Integrated sensor applications*

Plasma and reactive ion etch processes useful for PDMS patterning are well-known [12]. We have verified that these oxygen / fluorine based processes work equally well on the MWCNT/PDMS composites presented here.

Thus, it is possible to pattern the MWCNT / PDMS composites for use in an integrated sensor or other MEMS. In our laboratories, a MWCNT / PDMS composite based 'artificial skin' is under development.

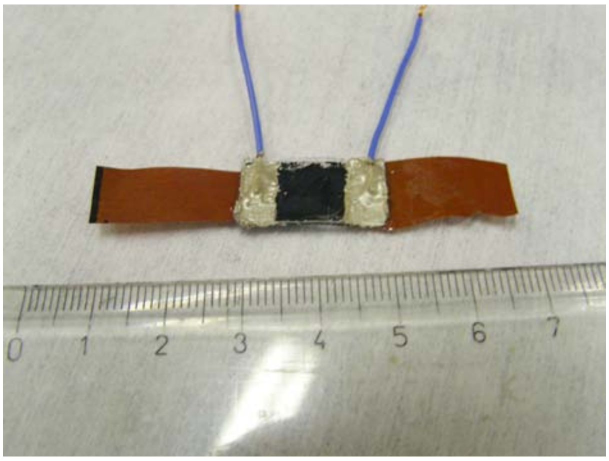

Figure 3: photograph of a VACNT / PDMS composite test sample

However, especially when finer sensor structures are required, the VACNT composites have clear advantages. First, as the VACNTs can be grown in situ on spots defined by lithography, patterning by etching is often not required. Their most significant advantage is their excellent regularity, which is especially important for limiting the variations in small sensor structures.

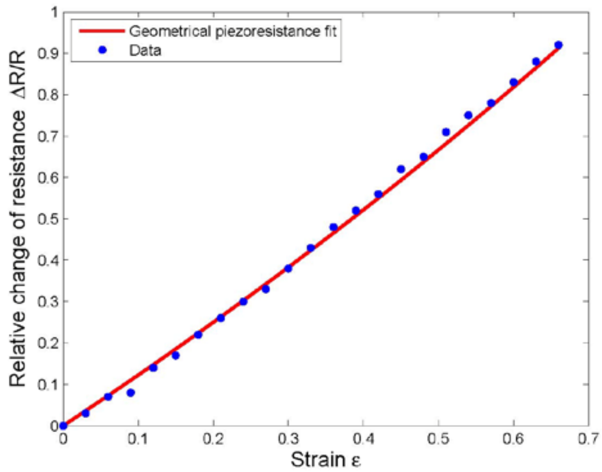

Figure 4: Measured piezoresistive behavior of VACNT / PDMS composites

On the negative side, the gauge factors found are inferior than those naturally present in silicon or even polysilicon. Therefore, we do not expect these composite materials to be used to replace silicon in classic MEMS devices such as pressure sensors unless major inprovements are achieved.

However, when the fabrication cost of relatively large areas of VACNTs becomes acceptable, we do see a future for these composite materials in large-area flexible organic electronics, e.g. in artificial skin or intelligent textile.

IV – Conclusions

This paper reports the fabrication and electromechanical characterization of carbon nanotube composites based on polydimetylsiloxane (PDMS). MWCNT/PDMS composites show a quasi-linear piezoresistive response with gauge factors between 0.8 and 2.3. However, the still inhomogeneous dispersion and presence of larger clusters results in a large variability.

Vertically aligned carbon carbon nanotubes can be considered as an easy way to get uniform dispersions of aligned carbon nanotubes in polymers approaching the ideal morphology. VACNT/PDMS composites show a linear piezoresistivity up to high strain values and a gauge factor of 1.4.

A model considering geometrical change of the sample only fits well on the measured piezoresistive behavior if a vertical Poisson ratio of 0.2 is assumed. This is a reasonable assumption given the presence of reinforcing vertically aligned fibers in the composite material.

Although the current gauge factor for VACNT/PDMS composites is lower than for commercial strain gauges (gauge factors around 2), vertically aligned carbon nanotubes composites have the potential to generate uniform localized CNT composites, a requirement for application in MEMS.

Further research should go to the influence of length, density and diameter of the vertically aligned carbon nanotubes on the piezoresistivity of the VACNT polymer composites.

Acknowledgements

Our sincere thanks go to Imec vzw and the University of Michigan for supplying VACNT covered substrates.

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